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Infrastructure Water Environment Buildings

Draft Reassessment of PCBs as the COC for the Kalamazoo River Superfund Site

November 28, 2012

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Outline

- Background
- Purpose and Objectives of the Reassessment
- Non-PCB Data Summary
- COPC Screening Evaluation
  - Approach
  - Dioxin/Furan TEQ Data
  - Co-occurrence with PCBs
  - Comparison to OUs and Morrow Lake
  - Risk Screening
- Conclusions

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Background

- Site was listed on NPL due to PCB levels in fish
- The Site is listed as a Great Lakes Area of Concern due to PCBs
- Recognition of PCBs as the risk driver has guided RI/FS work at the Site since the mid-1980s
  - USEPA-approved Site-wide Ecological and Human Health Risk Assessments focus on PCBs
- The scope of all completed remedial actions at the Superfund Site have been determined based on PCBs
- Non-PCB constituents have been analyzed in multiple sampling programs – PCBs have remained the focus of continued work
- USEPA requested that SRI/FS documents address other contaminants to justify the continued focus on PCBs

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COCs and COPCs

- **Chemicals (or constituents) of concern (COCs)** are the hazardous substances, pollutants, and contaminants that, at the end of the risk assessment, are found to be the risk drivers or those that may actually pose unacceptable human or ecological risks. The COCs typically drive the need for a remedial action (USEPA, 1999)[1].
- **Chemicals (or constituents) of potential concern (COPCs)** generally comprise the hazardous substances, pollutants, and contaminants that are investigated during the baseline risk assessment. The list of COPCs may include all of the constituents whose data are of sufficient quality for use in the quantitative risk assessment, or a subset thereof (USEPA, 1989)[2].

1. U.S. Environmental Protection Agency (EPA). 1999. A Guide to Preparing Superfund Proposed Plans, Records of Decision, and Other Remedy Selection Decision Documents. Office of Emergency and Remedial Response. Washington, DC. OSWER 9200.1-23.P.
2. U.S. Environmental Protection Agency (EPA). 1989. Risk Assessment Guidance for Superfund (RAGS): Volume I: Human Health Evaluation Manual (HHEM). (Part A). Interim Final. Office of Emergency and Remedial Response. Washington, DC. EPA 540/1-89/002. OSWER 9285.70-02B.

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Purpose of the Reassessment

- A Site-wide white paper "***Reassessment of PCBs as the COC for the Kalamazoo River Superfund Site***" is in development for USEPA review
- Purpose: Evaluate available data for non-PCB constituents, including dioxin/furans to reassess PCBs as the COCs for continuing SRI/FS work

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Objectives of the Reassessment

- Compile and present non-PCB constituent data from SRI and pre-SRI sampling
  - Summarize data by media, area, & depth intervals/sample type
- Present comparison to available criteria and screening values (update Area 1 SRI Appendix M with additional Area 2 data)
- Present comparison to data from landfill OUs and Morrow Lake
- Assess co-location with PCBs
- Conduct risk screening for constituents not screened out based on comparison to criteria, landfill OU data, and Morrow Lake
- Document reassessment outcomes

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NON-PCB DATA SUMMARY

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Non-PCB Analytical Samples for OU5

Program	Sediment/ Exposed Sediment	Soil
1993/94 RI	36	12
2000 RI	0	0
2001 USEPA sampling	16	4
2007-09 Area 1 SRI	36	0
2011 Area 2 SRI	41	140
Total	129	156

Program	Fish	Other Biota
1993/94 RI (whole-body, fillet, remaining carcass)	327	2
1993-1996 Michigan Dept. Community Health Sampling	25	0
1994-2009 Michigan Fish Contaminant Monitoring Program whole body carp in Lake Allegan	80	0
2001-2011 MDEQ LTM fish samples	122	0
Total	554	2

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Sediment and Exposed Sediment Dataset

- Includes sediment and exposed sediment samples collected from the following Areas of the Kalamazoo River:
  - Area 1: 38 Kalamazoo River and 18 Portage Creek samples
  - Area 2: 50 samples
  - Area 3: 7 samples
  - Area 4: 5 samples
  - Area 5: 7 samples
  - Area 6: 4 samples

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Non-PCB Analytical Samples from other Operable Units of the Site

Program	Samples of Soils and Residuals
12th Street Landfill OU	12
Allied Paper, Inc. Landfill OU	29
King Highway Landfill OU	14
Willow Boulevard/A-Site Landfill OU	19
Simpson Plainwell Paper Mill	1
Total	**75**

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COPC SCREENING EVALUATION

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Major Elements of the Approach

- Data screening evaluation based on detection frequency and pertinent criteria and guidelines
- Comparison to data from other OUs of the Site and Morrow Lake
- Evaluation of co-occurrence of those constituents that were not screened out
- Risk screening for those constituents not screened out
- Source considerations

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Approach to Non-PCB Screening Evaluation

- Frequency of detection in soil or residuals and sediment samples
  - Non-PCB constituents detected < 10% were not evaluated further
- Compare to criteria and guidelines:
  - Michigan regional soil background values
  - Sediment quality guidelines that reflect threshold effect concentrations (TECs)
  - Sediment quality guidelines that reflect probable effect concentrations (PECs)
  - USEPA Region 5 Ecological Screening Levels (ESLs)
  - Those below screening levels not further evaluated
- Evaluate biocumulative compound concentrations in biota
  - If exceed screening levels in sediment , but are below pertinent thresholds in biota, constituent not further evaluated

Screening to soil values

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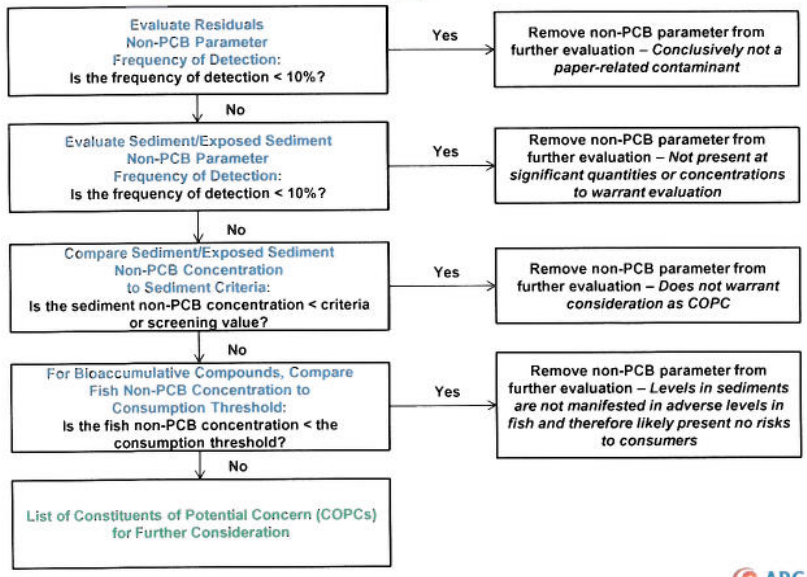
Screening Methodology



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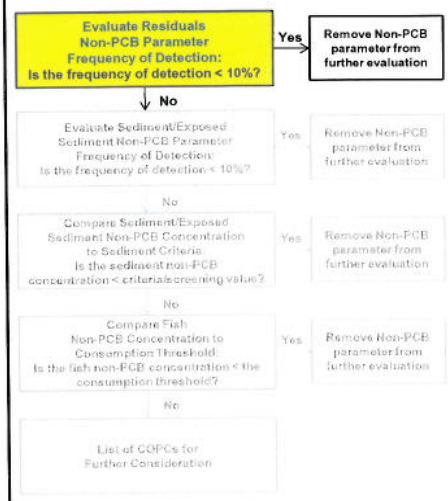
Frequency of Detection in Residuals Samples



- Total of 39 non-PCB constituents were detected in more than 10% of residuals samples and retained for further evaluation

Dioxins/Furans		
Total 2,3,7,8-TCDD TEQ		
Pesticides		
4,4'-DDE	Aldrin	Gamma-Chlordane
4,4'-DDT	Endrin Aldehyde	
Inorganics		
Aluminum	Cobalt	Mercury
Arsenic	Copper	Nickel
Barium	Cyanide	Selenium
Beryllium	Iron	Vanadium
Cadmium	Lead	Zinc
Chromium	Manganese	
Semivolatiles		
2-Methylnaphthalene	bis(2-Ethylhexyl)phthalate	Phenanthrene
4-Methylphenol	Naphthalene	
Volatiles		
2-Butanone	Carbon Disulfide	Tetrachloroethene
4-Methyl-2-pentanone	Chloroform	Toluene
Acetone	Ethylbenzene	Xylenes (total)
Benzene	Methylene Chloride	

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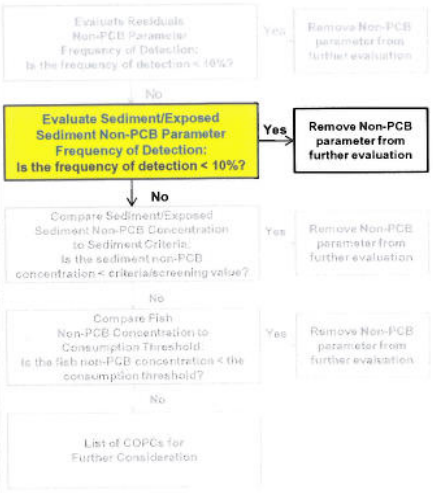
Frequency of Detection in Sediment/Exposed Sediment Samples



- 33 of the 39 non-PCB constituents detected in more than 10% of residuals sample were also detected in more than 10% of sediment samples and retained for further evaluation

Dioxins/Furans		
Total 2,3,7,8-TCDD TEQ		
Pesticides		
4,4'-DDE	Endrin Aldehyde	
4,4'-DDT	Gamma-Chlordane	
Inorganics		
Aluminum	Cobalt	Nickel
Arsenic	Copper	Selenium
Barium	Iron	Vanadium
Beryllium	Lead	Zinc
Cadmium	Manganese	
Chromium	Mercury	
Semivolatiles		
2-Methylnaphthalene	bis(2-Ethylhexyl)phthalate	Phenanthrene
4-Methylphenol	Naphthalene	
Volatiles		
2-Butanone	Carbon Disulfide	Toluene
Acetone	Methylene Chloride	
Benzene	Tetrachloroethene	

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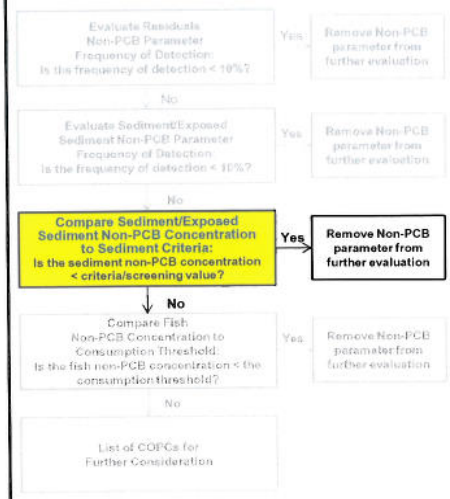
Compare Sediment/Exposed Sediment Results to Screening Criteria



- Sediment/exposed sediment data compared to Statewide Default Soil Background Levels (available for inorganics) and lowest of:
  - Consensus-Based TEC
  - Consensus-Based PEC
  - Ecological Screening Levels
- Modification to Area 1 SRI Appendix M approach – that consisted of a point-by-point comparison to all criteria
- Single-sample hypothesis test (Wilcoxon signed rank test) used to compare sediment mean concentrations to selected criteria
  - Null hypothesis H_o: sediment median result ≥ background/screening level result (Form 2)
  - Hypothesis test conducted using USEPA ProUCL (v. 4.1.01) software

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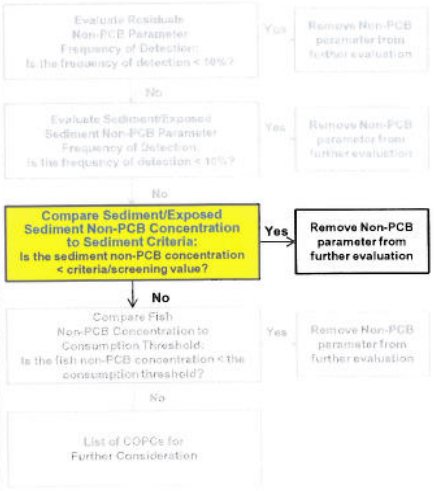
Compare Sediment/Exposed Sediment Results to Screening Criteria (cont.)



- Concentrations of 10 of the 33 non-PCB constituents were less than screening criteria – these were dropped
- Concentrations of 23 of the 33 non-PCB constituents exceeded screening criteria – these were retained for further evaluation

Dioxins/Furans		
Total 2,3,7,8-TCDD TEQ		
Pesticides		
4,4'-DDE	4,4'-DDT	Gamma-Chlordane
Inorganics		
Aluminum	Chromium	Selenium
Arsenic	Copper	Vanadium
Barium	Iron	Zinc
Beryllium	Lead	
Cadmium	Mercury	
Semivolatiles		
2-Methylnaphthalene	bis(2-Ethylhexyl)phthalate	Phenanthrene
4-Methylphenol	Naphthalene	
Volatiles		
Acetone		

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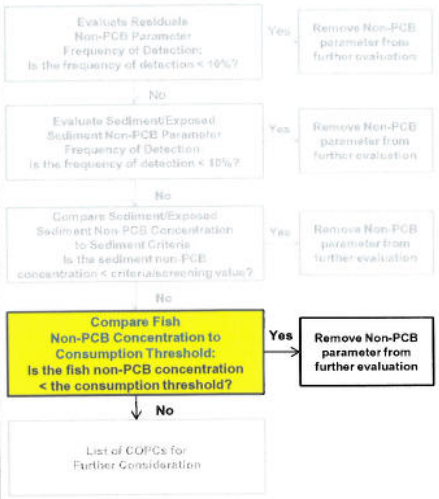
Compare Fish Results to MDCH Thresholds



- Non-PCB results from the most recent sampling events used for comparison
  - 2011 Trowbridge Carp Fillets (11 samples)
    - Total 2,3,7,8-TCDD TEQ
  - 2009 Lake Allegan Whole-Body Carp (10 samples)
    - Total DDT
    - Total Chlordane
    - Mercury
- Non-PCB constituents in fish were compared to MDCH Threshold Values used to establish Sport Fish Consumption Advisories

Constituent	MDCH Trigger Level
Total Chlordane	0.3 mg/kg
Total DDT	5.0 mg/kg
Mercury	0.5 mg/kg (restricted consumption)
	1.5 mg/kg (no consumption)
2,3,7,8-TCDD TEQ	10 ng/kg

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2011 MDEQ Carp Samples: Dioxin/Furan Total TEQ

	Dioxin/Furan TEQ (ng/kg)	
Location	**Maximum**	**Average**
ABSA 3 - Near Kalamazoo Avenue	3.2	1.6
ABSA 8 - Former Trowbridge Impoundment	3.1	1.7
ABSA 11 - Near New Richmond	3.1	1.7

33 Carp Samples – 11 from Each Location

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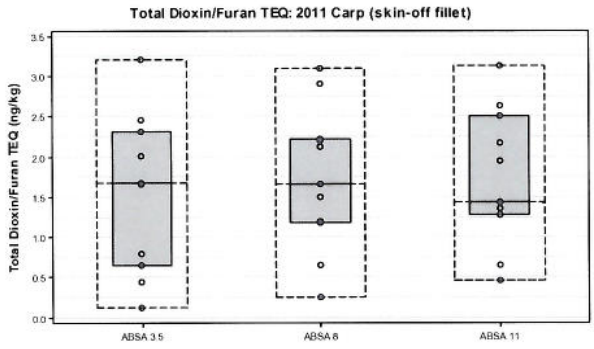
2011 MDEQ Carp Samples: Dioxin/Furan Total TEQ



33 Carp Samples – 11 from Each Location

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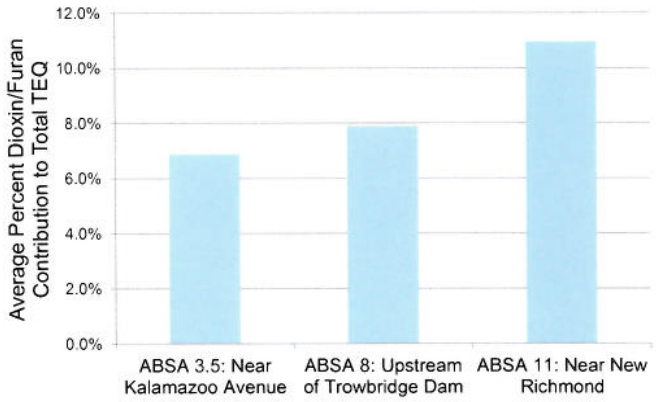
2011 MDEQ Carp Samples: Dioxin/Furan Contribution to Total TEQ



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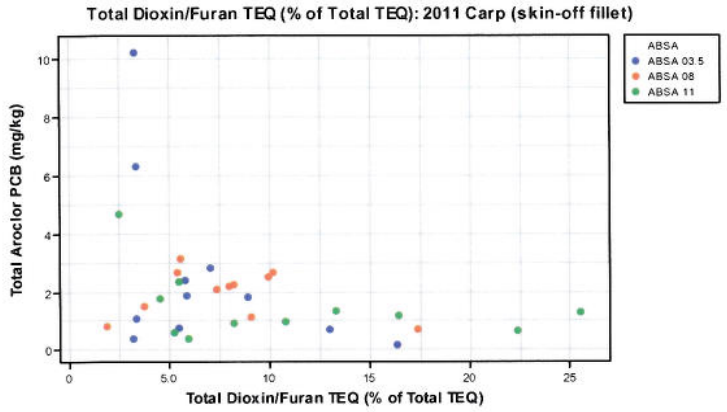
2011 MDEQ Carp Samples:
Total PCB vs. Percent Dioxin/Furan Contribution to Total TEQ



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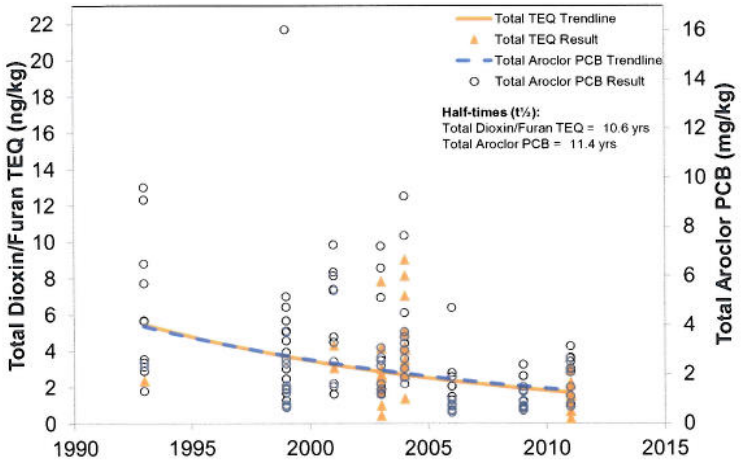
ABSA 8 Carp TEQ Time Trend



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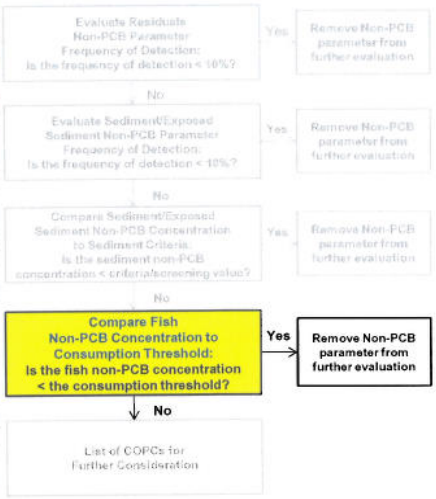
Compare Fish Results to MDCH Thresholds (cont.)



- Fish samples not analyzed for inorganics (except mercury), SVOCs, or VOCs
- Single-sample hypothesis test (Wilcoxon signed rank test) used to compare fish mean concentrations to threshold values
  - Null hypothesis H_o: sediment median result ≥ background/screening level result (Form 2)
  - Hypothesis test conducted using USEPA ProUCL (v. 4.1.01) software
- Mean concentrations of Total 2,3,7,8-TCDD TEQ[1], Mercury, Total DDT, and Total Chlordane in fish were less than MDCH threshold values

1. TEQ evaluated based on dioxin and furan constituents only

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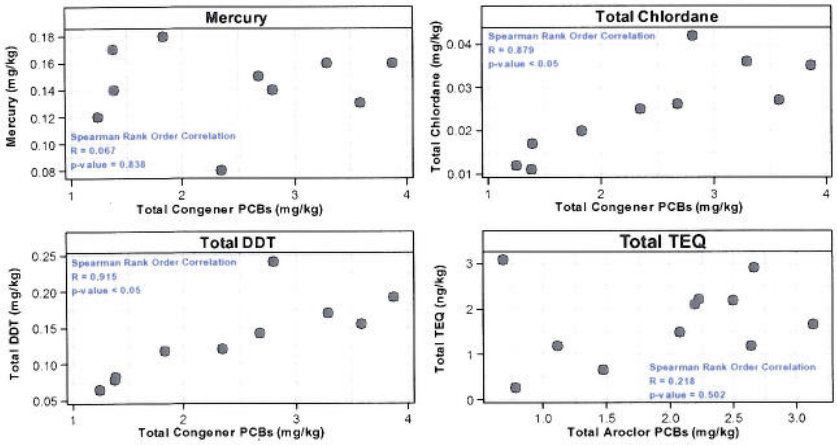
Non-PCB vs. Total PCB in Fish Samples



- Non-PCB and PCB results from the following sampling events
  - 2011 Trowbridge Carp Fillet (11 samples)
    - Total TEQ
  - 2009 Lake Allegan Whole-body Carp (10 samples)
    - Total DDT
    - Total Chlordane
    - Mercury
- Total PCBs significantly correlated with Total Chlordane and Total DDT (4,4)
- Total PCBs not correlated with Mercury and Total TEQ
- Spearman Rank Order Correlation test conducted using SigmaPlot (Version 12) software.

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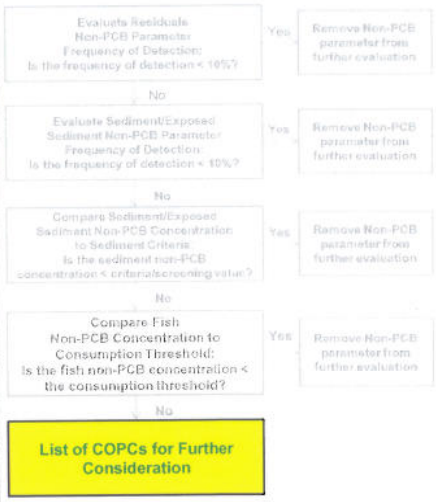
Non-PCB COPCs Further Considered



- Based on the results of the non-PCB evaluation, the following constituents are retained for further consideration:

Inorganics		
Aluminum	Cadmium	Lead
Arsenic	Chromium	Selenium
Barium	Copper	*Vanadium*
Beryllium	Iron	Zinc

Semivolatiles	
2-Methylnaphthalene	Naphthalene
4-Methylphenol	Phenanthrene
bis(2-Ethylhexyl)phthalate	

Volatiles
Acetone

Note: Constituents in italics have no criteria for comparison.

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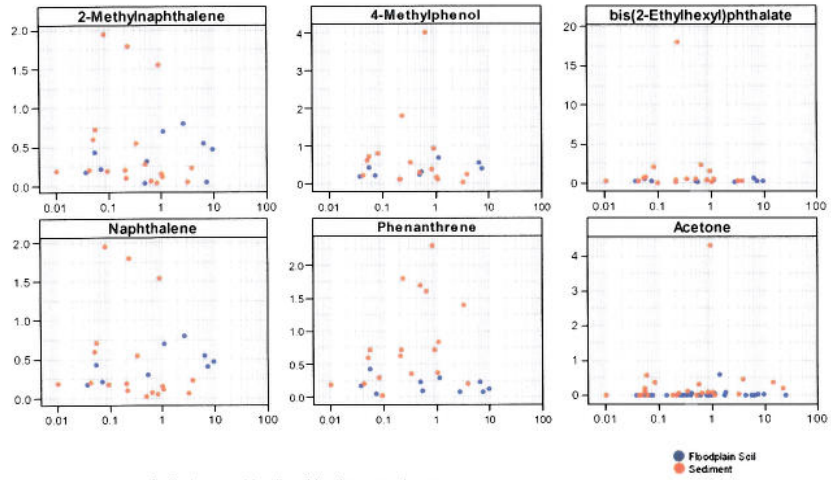
Sediment and Exposed Sediment Co-Occurrence of Non-PCB and Total PCB*



*Constituents retained for further consideration following screening process

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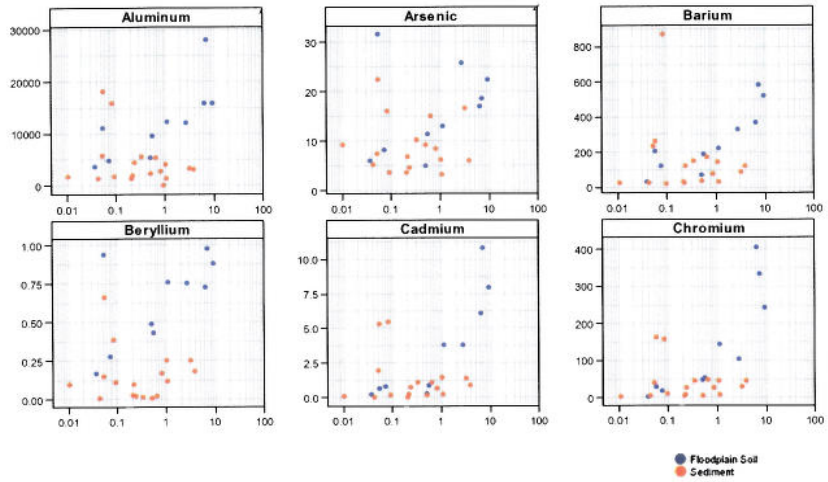
Sediment and Exposed Sediment Co-Occurrence of Non-PCB and Total PCB (cont.)*



*Constituents retained for further consideration following screening process

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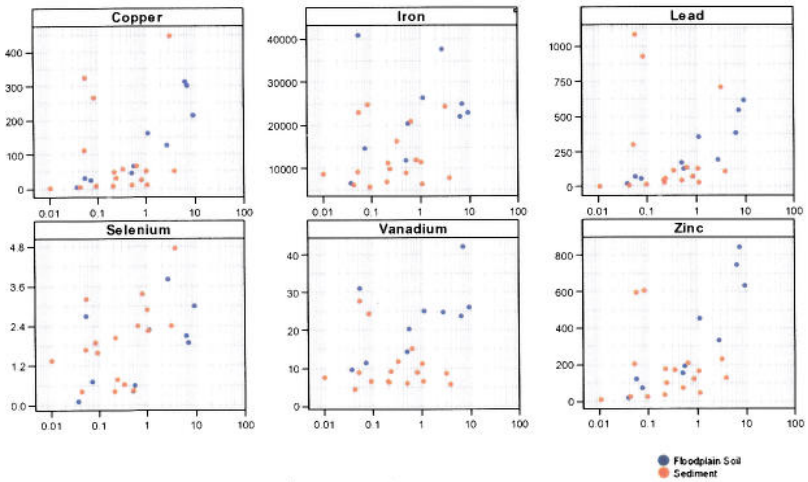
Sediment and Exposed Sediment Co-Occurrence of Non-PCB and Total PCB (cont.)*



*Constituents retained for further consideration following screening process

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Inorganics vs. Statewide Default Soil Background Levels

Parameter Group	Constituent	Range (mg/kg)	Arithmetic Mean (mg/kg)	Median (mg/kg)	95% UCL (mg/kg)	Statewide Default Soil Background Levels[a,b]			
						Criteria (mg/kg)	Mean Ratio to Criteria	Median Ratio to Criteria	95% UCL Ratio to Criteria
Inorganics	Aluminum	1,300 - 28,000	6700	4200	8100	6900	0.97	0.60	1.2
	Arsenic	1.0 B - 67	12	10	14	5.8	2.0	1.8	2.3
	Barium	11 B - 1,000	210	120	260	75	2.8	1.7	3.5
	Beryllium	0.020 U - 1.9	0.31	0.17	0.39	--	--	--	--
	Cadmium	0.060 U - 13 [10]	2.5	1.0	4.0	1.2	2.1	0.86	3.3
	Chromium	3.5 - 450	80	35	120	--	--	--	--
	Copper	1.4 B - 500	120	54	160	32	3.8	1.7	4.9
	Iron	1,100 - 26,000 [25,000]	12000	10000	13000	12000	1.0	0.87	1.1
	Lead	1.9 U - 1,300 [1,100]	310	141	470	21	15	6.7	23
	Selenium	0.77 U - 9.4	1.7	1.3	1.6	0.41	4.1	3.2	3.9
	Vanadium	4.5 B - 42	14	11	18	--	--	--	--
	Zinc	9.5 - 950	270	180	330	47	5.7	3.8	7.0

Note:

a. MDEQ 2011. Revised Part 201 Cleanup Criteria and Part 213 Risk-based Screening Levels. Attachment 1. Tables 1, 2, and 3. http://www.michigan.gov/deq/0,1607,7-135-3311_4109_9846_30022-251790--,00.html

b. Grey shaded cells indicate ratios > 1, and blue shaded cells indicate ratios > 10.

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Comparison of Non-PCB COPCs Further Considered to Paper Residuals Data

- Basis: Unless concentrations of COPCs in paper residuals are shown to be higher than concentrations in sediments and soils, paper residuals cannot be either a significant or primary source
  - Dilution by watershed derived sediments will result in lower concentrations in the former impoundment sediments than in the landfills

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Residuals and Sediment/Exposed Sediment Non-PCB COPCs Summary Statistics

Parameter Group	Constituent	Residuals		Sediment	
		Frequency of Detection	Range	Frequency of Detection	Range
Inorganics (mg/kg)	Aluminum	63/63 (100%)	3,000 - 22,000	80/80 (100%)	1,300 - 28,000
	Arsenic	60/63 (95.2%)	0.48 U - 9.5	80/80 (100%)	1.0 B - 67
	Barium	61/63 (96.8%)	14 U - 1,300 * [1,300 *]	80/80 (100%)	11 B - 1,000
	Beryllium	10/63 (15.9%)	0.17 U - 2.4	68/80 (85.0%)	0.020 U - 1.9
	Cadmium	13/63 (20.6%)	0.44 U - 3.7	69/80 (86.2%)	0.060 U - 13 [10]
	Chromium	63/63 (100%)	6.2 - 210	80/80 (100%)	3.5 - 450
	Copper	63/63 (100%)	18 * - 280 JN*	80/80 (100%)	1.4 B - 500
	Iron	63/63 (100%)	440 * - 11,000 *	80/80 (100%)	1,100 - 26,000 [25,000]
	Lead	63/63 (100%)	4.9 N* - 1,400	79/80 (98.8%)	1.9 U - 1,300 [1,100]
	Selenium	14/63 (22.2%)	0.19 UJW - 3.1	40/80 (50.0%)	0.77 U - 9.4
	Vanadium	63/63 (100%)	4.9 B - 25	80/80 (100%)	4.5 B - 42
	Zinc	56/56 (100%)	31 N* - 1,100 J	80/80 (100%)	9.5 - 950
Semivolatiles (mg/kg)	2-Methylnaphthalene	47/63 (74.6%)	0.68 U - 22 J	35/81 (43.2%)	0.20 U - 1.5
	4-Methylphenol	37/61 (60.7%)	0.60 U - 38	32/72 (44.4%)	0.20 U - 6.2
	bis(2-Ethylhexyl)phthala	38/63 (60.3%)	0.68 U - 15 J	40/81 (49.4%)	0.19 UBJ - 18
	Naphthalene	19/63 (30.2%)	0.68 U - 29	35/81 (43.2%)	0.20 U - 1.4
	Phenanthrene	16/63 (25.4%)	0.68 U - 7.2 J	68/81 (84.0%)	0.27 U - 31 D
Volatiles (mg/kg)	Acetone	43/63 (68.3%)	0.014 U - 4.1 J	76/109 (69.7%)	0.0048 U - 2.0 DJ [1.9 D]

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Comparison of Non-PCB COPCs in Residuals and Sediment and Soil/Exposed Sediment Samples

- Non-PCB results in residuals samples were compared to sediment/exposed sediment samples to determine if concentrations were higher in residuals
- Two-sample hypothesis test (Gehan or Wilcoxon-Mann-Whitney tests) used to compare mean concentrations in residuals and sediment/exposed sediment
  - Null hypothesis H_o: residual median result ≥ sediment/exposed sediment median result (Form 2)
  - Hypothesis test conducted using USEPA ProUCL (v. 4.1.01) software
- Residuals concentrations of arsenic, beryllium, cadmium, iron, and selenium were not statistically significantly higher than sediment/exposed sediment concentrations

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Comparison of Non-PCB COPCs Further Considered to Morrow Lake Sediment Data

- Morrow Lake data comprised of sediment samples collected as part of Enbridge Oil Spill Monitoring effort
  - 367 samples collected from 58 sediment locations between July and October 2010
  - Most recent sample result from each location used for comparison
- Two-sample hypothesis test (Gehan or Wilcoxon-Mann-Whitney tests) used to compare mean concentrations in sediment downstream and upstream of Morrow Dam
  - Null hypothesis H_0: downstream median result ≥ upstream median sediment result (Form 2)
  - Hypothesis test conducted using USEPA ProUCL (v. 4.1.01)

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Comparison of Non-PCB COPCs Further Considered to Morrow Lake Data (cont.)

- Site sediment/exposed sediment concentrations of acetone, arsenic, beryllium, chromium, and iron were not statistically significantly higher than sediment samples collected as part of Enbridge Oil Spill Monitoring effort in Morrow Lake
  - Aluminum was not analyzed in Enbridge Oil Spill Monitoring sediment samples
  - 2-Methylnaphthalene, 4-Methylphenol, and naphthalene were not evaluated due to low frequency of detection in Enbridge Oil Spill Monitoring sediment samples in Morrow Lake

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Results of Residuals and Morrow Lake Data Comparisons

- Based on comparison to paper residuals...

Inorganics		
Aluminum	~~Cadmium~~	Lead
~~Arsenic~~	Chromium	~~Selenium~~
Barium	Copper	*Vanadium*
~~*Beryllium*~~	~~Iron~~	Zinc
Semivolatiles		
2-Methylnaphthalene	Naphthalene	
4-Methylphenol	Phenanthrene	
bis(2-Ethylhexyl)phthalate		
Volatiles		
Acetone		

Note: Constituents in italics have no criteria for comparison.

- Based on comparison to paper residuals and Morrow Lake from Enbridge data set...

Inorganics		
Aluminum	~~Cadmium~~	Lead
~~Arsenic~~	~~Chromium~~	~~Selenium~~
Barium	Copper	*Vanadium*
~~*Beryllium*~~	~~Iron~~	Zinc
Semivolatiles		
2-Methylnaphthalene	Naphthalene	
4-Methylphenol	Phenanthrene	
bis(2-Ethylhexyl)phthalate		
Volatiles		
~~Acetone~~		

Note: Constituents in italics have no criteria for comparison. Those in gray font were not analyzed for in Enbridge data set, preventing comparison to upstream concentrations.

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Human Health Risk Screening Approach for Non-PCB COPCs Further Considered

- Use all available soil data from 1993 – present
- Use both residential and industrial/commercial screening values, although only non-residential exposures are foreseeable in the formerly impounded areas
- Use 95%UCL on the mean for comparison to screening levels
- Use MDEQ Direct Contact Risk-Based Screening Levels (RBSLs) as screening criteria

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Human Health Risk Screening: Soil to MDEQ Direct Contact Residential Criteria

Analyte	Maximum Detect Conc. (mg/kg)	Median Detect Conc. (mg/kg)	95% UCL Conc. (mg/kg)	MDEQ Direct Contact Residential RBSL (mg/kg) (MDEQ 2012)	Ratio of Maximum Conc. in Soil/RBSL	Ratio of Median Conc. in Soil/ RBSL	Ratio of 95% UCL Conc. in Soil/ RBSL
Acetone	0.6	0.02	0.1	23,000	0.00003	0.000001	0.00001
Aluminum	27,900	11,600	15,970	50,000	0.6	0.2	0.3
Arsenic	31.6	15	21.1	7.6	4	2.0	3
Barium	585	213	371	37,000	0.02	0.006	0.01
Berylium	0.98	0.74	0.80	410	0.002	0.002	0.002
Bis(2- Ethylhexyl)phthalate	1.1	0.29	0.7	2,800	0.0004	0.0001	0.0002
Cadmium	10.9	2.6	5.8	550	0.02	0.005	0.01
Chromium, Total	408	79	222	2,500	0.16	0.03	0.09
Copper	314	94.55	195	20,000	0.02	0.005	0.01
Iron	41,100	22,450	29,081	160,000	0.3	0.1	0.2
Lead	617	184	377	400	2	0.5	1
2-Methylnaphthalene	1.6	0.75	1.1	8,100	0.0002	0.00009	0.0001
4-Methylphenol	1.4	0.73	1.0	11,000	0.0001	0.000066	0.00009
Naphthalene	1.6	0.85	1.1	16,000	0.0001	0.00005	0.0001
Phenanthrene	0.87	0.18	0.42	1,600	0.001	0.0001	0.0003
Selenium	3.8	2.0	2.5	2,600	0.001	0.001	0.001
Vanadium	42.1	24.5	28.6	750	0.06	0.03	0.04
Zinc	846	267	533	170,000	0.005	0.002	0.003

= Maximum detected concentration and/or 95% UCL is greater than MDEQ Direct Contact Residential RBSL
= Ratio of constituent concentration to screening level exceeds 1

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Human Health Risk Screening: Soil to MDEQ Direct Contact Industrial Criteria

Analyte	Maximum Detect Conc. (mg/kg)	Median Detect Conc. (mg/kg)	95% UCL Conc. (mg/kg)	MDEQ Direct Contact Industrial RBSL (mg/kg) (MDEQ 2012)	Ratio of Maximum Conc. in Soil/ RBSL	Ratio of Median Conc. in Soil/ RBSL	Ratio of 95% UCL Conc. in Soil/ RBSL
Acetone	0.6	0.02	0.1	73,000	0.00001	0.0000002	0.000002
Aluminum	27,900	11,600	15,970	370,000	0.08	0.03	0.04
Arsenic	31.6	15	21.1	37.0	0.9	0.4	0.6
Barium	585	213	371	130,000	0.005	0.002	0.003
Berylium	0.98	0.74	0.80	1,600	0.0006	0.0005	0.0005
Bis(2-Ethylhexyl)phthalate	1.1	0.29	0.7	10,000	0.0001	0.00003	0.00007
Cadmium	10.9	2.6	5.8	2,100	0.005	0.001	0.003
Chromium, Total	408	79	222	9,200	0.04	0.009	0.02
Copper	314	94.55	195	73,000	0.004	0.001	0.003
Iron	41,100	22,450	29,081	580,000	0.1	0.04	0.1
Lead	617	184	377	900	0.7	0.2	0.4
2-Methylnaphthalene	1.6	0.75	1.1	26,000	0.00006	0.00003	0.00004
4-Methylphenol	1.4	0.73	1.0	36,000	0.00004	0.00002	0.00003
Naphthalene	1.6	0.85	1.1	52,000	0.00003	0.00002	0.00002
Phenanthrene	0.87	0.18	0.42	5,200	0.0002	0.00003	0.00008
Selenium	3.8	2.0	2.5	9,600	0.0004	0.00021	0.0003
Vanadium	42.1	24.5	28.6	5,500	0.008	0.004	0.005
Zinc	846	267	533	630,000	0.001	0.0004	0.0008

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Eco Risk Screening Approach

- Initial screening values were either the original Eco-SSL (USEPA 2012) values for soil or PEC values from MacDonald et al. (2000) for sediment
- Alternate soil screening values were based on revised Eco-SSL values calculated using the geomean of the NOAEL and LOAEL, or the LOAEL values for TRVs
- Geomean Alternate Screening Value was calculated using the geomean of the NOAEL and LOAEL values as the TRV in the equation provided in the Eco-SSL (USEPA 2012) documents for avian species and mammals [HQ = FIR*(Soil*Ps+Bi)/TRV solved for HQ=1 where Soil = Eco SSL]
- LOAEL Alternate Screening Value was calculated using the LOAEL value as the TRV in the equation provided in the Eco-SSL document for avian species and mammals
- The most conservative LOAEL based Eco-SSL (for avian species or mammals) was selected as the Alternate Screening Value for cadmium, chromium, copper, lead, selenium, vanadium, and zinc
- The max, median, and 95% UCL concentrations were then divided by the selected screening value to determine the max, median and 95% UCL quotients

MacDonald et al. 2000. Development and Evaluation of Consensus-Based Sediment Quality Guidelines for Freshwater Ecosystems. Arch. Environ. Contam. Toxicol. 39, 20–31.
USEPA 2012. Ecological Soil Screening Level documents available at: http://www.epa.gov/ecotox/ecossl/

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Risk Screening of Non-PCB COPCs Further Considered – **Sediment** Screening Criteria

Contaminant	Sediment Screening Values				
	EPA R3 (mg/kg)	EPA R4 (mg/kg)	EPA R5 (mg/kg)	MacDonald (2000) (mg/kg) TEC	PEC
2-methyl naphthalene	0.0202	0.33	0.0202	0.176[b]	0.561[b]
4-methyl phenol	0.67	--	0.0554	--	--
Bis(ethylhexyl)phthalate	0.182	0.182	0.182	--	--
naphthalene	0.176	0.33	0.176	0.176	0.561
phenanthrene	0.204	0.33	0.204	0.204	1.17
acetone	--	--	7.8	--	--
Aluminum	--	--	--	--	--
Arsenic	9.8	7.24	9.79	9.79	33
Barium	--	--	--	--	--
Berylium	--	--	--	--	--
Cadmium	1	0.676	1	0.99	4.98
Chromium*	43.4	52.3	43.4	43.4	111
Copper	31.6	18.7	31.6	31.6	149
Iron	20000	--	--	--	--
Lead	35.8	30.2	35.8	35.8	128
Selenium	2	--	--	2.5[a]	4[a]
Vanadium	--	--	--	--	--
Zinc	121	124	121	121	459

Notes:
a. From NIWQP (1998)
b. Naphthalene used as surrogate
* Trivalent chromium

= Selected Value

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Risk Screening of Non-PCB COPCs Further Considered – **Sediments**

- Screening of 2011 Surface Sediment Samples from Area 2

Parameter Group	Analyte	N	Range	Screening Level	Samples Exceeding	Max Detect Conc. (mg/kg)	Max Conc. Quotient	Median Conc. (mg/kg)	Median Conc. Quotient	95% UCL (mg/kg)	95% UCL Quotient
Inorganics	Aluminum	18	0-18,100	--	--	18,100	--	2865	--	9430	--
	Arsenic	17	3.3-22.4	33	0/17	22.4	0.68	7.15	0.22	11.74	0.36
	Barium	17	18.8-87.3	--	--	873	--	81	--	234	--
	Beryllium	17	0.02-0.663	--	--	0.663	--	0.105	--	0.245	--
	Cadmium	17	0.07-5.5	4.98	2/17	5.5	1.10	0.76	0.15	2.24	0.45
	Chromium	17	4.7-164	111	2/17	164	1.48	29.2	0.26	66.25	0.60
	Copper	17	1.8-448	149	3/17	448	3.01	47.1	0.32	170.6	1.14
	Iron	17	5,710-24,800	--	--	24,800	--	9730	--	15714	--
	Lead	17	2.6-1,090	128	6/17	1,090	8.52	69.9	0.55	437	3.41
	Selenium	17	0.85-9.5	4	7/17	9.5	2.38	2.7	0.68	4.54	1.14
	Vanadium	17	4.5-27.7	--	--	27.7	--	8.6	--	13.17	--
	Zinc	17	13.2-606	459	2/17	606	1.32	129	0.28	272.4	0.59
Semivolatiles	2-methyl naphthalene	18	0.037-3.9	0.561	6/18	3.9	6.95	0.405	0.72	1.701	3.03
	4-methylphenol	16	0.029-4.0	0.0554	15/16	4	72.20	0.51	9.21	1.672	30.18
	Bis(ethylhexyl)phthalate	18	0.031-18	0.182	17/8	18	98.9	0.45	2.5	6.07	33.4
	Naphthalene	18	0.034-3.9	0.561	6/18	3.9	6.95	0.395	0.70	1.7	3.03
	Phenanthrene	18	0.026-3.6	1.17	6/18	3.6	3.08	0.63	0.54	1.48	1.26
Volatiles	Acetone	24	0.0006-8.6	7.8	1/24	8.6	1.10	0.1045	0.01	2.037	0.26

= Value greater than 2.0

N – number of samples
Max Conc. Quotient = Max Detect Conc/Screening Level
Median Conc. Quotient = Median Conc./Screening Level
95% UCL Quotient = 95% UCL/Screening Level

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Risk Screening of Non-PCB COPCs Further Considered – **Soil** Screening Criteria

Contaminant	Soil Screening Values						
	Eco SSL (mg/kg dw)				ORNL (Effroymsen 1997a,b)		
	Plant	Soil Invert	Bird	Mammal	Worm	Micro Org	Terr Plant
2-methyl naphthalene	--	--	--	--	--	--	--
4-methyl phenol	--	--	--	--	--	--	--
Bis(ethylhexyl)phthalate	--	--	--	--	--	--	--
Naphthalene	--	--	--	--	--	--	--
Phenanthrene	--	--	--	--	--	--	--
Acetone	--	--	--	--	--	--	--
Aluminum	N/A[a]	N/A[a]	N/A[a]	N/A[a]	--	600	50
Arsenic	18	--	43	--	60	100	10
Barium	--	330	--	2000	--	3000	500
Beryllium	--	40	--	21	--	--	10
Cadmium	32	140	4.4	6.5	20	20	4
Chromium*	--	--	26	137	0.4	10	1
Copper	70	80	84	82	50	100	100
Iron	--	--	--	--	--	200	--
Lead	120	1700	26	122	500	900	50
Selenium	0.52	4.1	3.2	1.1	70	100	1
Vanadium	--	--	15	552	--	20	2
Zinc	160	120	468	9050	200	100	50

= Selected Value

Notes:

* ecoSSL for trivalent chromium

a - According to Aluminum Eco-SSL document (USEPA 2003), aluminum is identified as a COPC only at sites where the soil pH is less than 5.5 -- this is below the pH values for the Kalamazoo Site

Efroymson, R.A., M.E. Will, G.W. Suter II, and A.C. Wooten. 1997a. *Toxicological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants: 1997 Revision*. Prepared for the Oak Ridge Laboratory. November.

Efroymson, R.A., M.E. Will, G.W. Suter II, and A.C. Wooten. 1997b. *Toxicological Benchmarks for Contaminants of Potential Concern for Effects on Soil and Litter Invertebrates and Heterotrophic Process: 1997 Revision*. Prepared for the Oak Ridge Laboratory. November.

USEPA 2003. Ecological Soil Screening Value for Aluminum available at http://www.epa.gov/ecotox/ecossl/pdf/eco-ssl_aluminum.pdf

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Risk Screening of Non-PCB COPCs Further Considered – **Soils**

- Screening of 2011 Surface Soil Samples from Area 2

Parameter Group	Analyte	N	Range	Screening Level (mg/kg)	Samples Exceeding	Max Detect Conc. (mg/kg)	Max Conc. Quotient	Median (mg/kg)	Median Conc. Quotient	95% UCL (mg/kg)	95% UCL Quotient
Inorganics	Aluminum	10	3,590-27,900	--	--	27,900	--	11,600	--	15,970	--
	Arsenic	10	5.1-31.6	18	4/10	31.6	1.76	15	0.83	21.07	1.17
	Barium	10	30.5-585	330	3/10	585	1.77	213	0.65	370.7	1.12
	Beryllium	10	0.17-0.98	40	0/10	0.98	0.02	0.74	0.02	0.804	0.02
	Cadmium	10	0.51-10.9	4.4	3/10	10.9	2.48	2.6	0.59	5.78	1.31
	Chromium	10	5.8-408	28	8/10	408	14.57	79.4	2.84	222.4	7.94
	Copper	10	3.8-314	82	5/10	314	3.83	94.55	1.15	195	2.38
	Iron	10	6,540-41,100	--	--	41100	--	22450	--	29081	--
	Lead	10	24.2-617	26	9/10	617	23.73	184	7.08	377	14.50
	Selenium	10	0.27-3.8	1.1	6/10	3.8	3.45	2	1.82	2.49	2.26
	Vanadium	10	9.7-42.1	15	7/10	42.1	2.81	24.45	1.63	28.6	1.91
	Zinc	10	23.3-846	468	3/10	846	1.81	266.5	0.57	532.6	1.14
Semivolatiles	2-methyl naphthalene	10	0.04-1.6	20	0/10	1.6	0.08	0.75	0.0375	1.05	0.0525
	4-methylphenol	8	0.35-1.4	--	--	1.4	--	0.725	--	1	--
	Bis(ethylhexyl)phthalate	12	0.066-1.1	1.1	0/12	1.1	1	0.29	0.26	0.665	0.60
	Naphthalene	10	0.029-1.6	20	0/10	1.6	0.08	0.845	0.042	1.097	0.055
	Phenanthrene	10	0.053-0.87	21	0/10	0.87	0.041	0.18	0.0086	0.423	0.020
Volatiles	Acetone	29	0.005-0.6	10	0/29	0.6	0.06	0.015	0.0015	0.13	0.013

N – number of samples
Max Conc. Quotient = Max Detect Conc/Screening Level
Median Conc. Quotient = Median Conc./Screening Level
95% UCL Quotient = 95% UCL/Screening Level

= Value greater than 2.0

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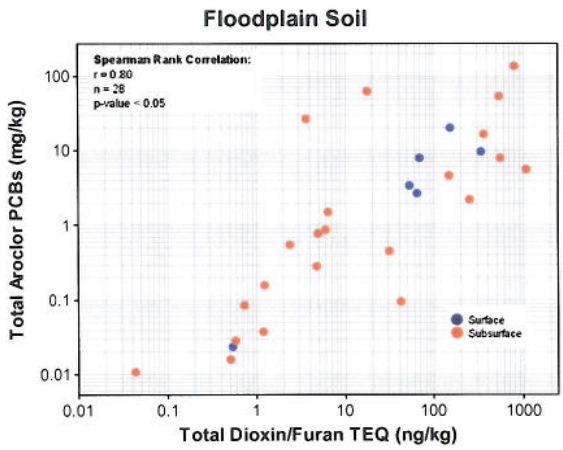
Soil Total PCB vs. Dioxin/Furan TEQ



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PRELIMINARY REASSESSMENT OUTCOMES

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COPC Reassessment Outcomes (1 of 3)

- Dioxin/furan TEQ concentrations in 33 carp samples collected in 2011 from three locations are all below the MDEQ consumption advisory threshold of 10 ppt (max = 3.1 ppt)
  - Indicates dioxin/furan levels in fish do not pose risks to anglers
- Dioxin/furan TEQ are low relative to PCBs
  - Average contribution to Total TEQ in fish is 7 to 11%
- Dioxin/furan TEQ in fish are correlated with Total PCB
  - Highest levels tend to be in fish with the most PCB
- Dioxin/furan levels in fish have declined over time
- Reductions of PCBs in fish tissue are likely to coincide with further reduction in dioxin/furan levels due to similar partitioning behavior

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COPC Reassessment Outcomes (2 of 3)

- Dioxin/furan TEQ in soils are correlated with Total PCBs due to similar partitioning behavior
- In comparison to MDEQ's generic residential soil criteria, the 95%UCL moderately exceeds (approximately a factor of 2), however the floodplains are not suited for residential development
- Based on co-location of higher PCB and dioxin/furan concentrations in soils, addressing higher levels of PCBs will also address higher dioxin/furan exposure levels

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COPC Reassessment Outcomes (3 of 3)

- Screening of non-PCB constituents identified 12 inorganic and 6 other organic chemicals for further consideration
- Risk screening indicates most of these compounds present no unacceptable risk
- In sediments:
  - 95%UCLs for lead, napthalene, and 2-methyl napthalene exceeded screening criteria by approximately a factor of 3
  - 4-methylphenol and bis-ethylhexylphalate exeeded by approximately 30 times
- In soils:
  - 95%UCLs for copper and selenium exceeded screening values by approximately 2.3 times
  - lead and chromium 95%UCLs were approximately 14.5 and 8 times greater, respectively

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Source Considerations

- Numerous potential continuing sources exist in the industrialized/ urbanized watershed as well as in rural areas for the several chemicals further considered that exceed screening values in soils and sediments. For example:
  - Industrial, urban and roadway stormwater
  - Wastewater treatment plants
  - Lead and napthalene are associated with gasoline, and numerous roadways, freeways, and filling stations exist in the surrounding urban areas
  - Copper is associated with roofing, piping, and electrical applications
  - Arsenic concentrations are known to be elevated in local soils
- The relatively low concentrations of these constituents are unlikely to warrant remedial consideration, and continuing source activity is expected, unrelated to historical paper-making

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Next Steps

- Agency review/feedback on reassessment approach by January 2013
- Submit White Paper for Agency review in February 2013
- Confirm whether or not any additional SRI characterization needs exist for non-PCB constituents

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